

Griffiths singularities in unbinding of strongly disordered polymers

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Griffiths singularities occurring in the unbinding of strongly disordered heteropolymers are studied. A model with two randomly distributed binding energies -1 and $-v$, is introduced and studied analytically by analyzing the Lee-Yang zeros of the partition sum. It is demonstrated that in the limit $v \rightarrow \infty$ the model exhibits a Griffiths type singularity at a temperature $T_G = O(1)$ corresponding to melting of long homogeneous domains of the low binding energy. For finite $v \gg 1$ the model is expected to exhibit an additional, unbinding, transition at a high temperature $T_M = O(v)$.

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The unbinding transition of two polymers has attracted considerable attention in recent years. This phenomenon arises in a variety of physical contexts in which two linearly extended objects interact. Examples are the denaturation transition of double stranded DNA [1] where the two strands of the molecule unbind; wetting in two dimensions [2] where the linear interface separating two bulk phases becomes unbound from the substrate; the depinning of flux lines from a columnar defect in type II superconductors [3] and others. In these problems an attractive interaction binds the two polymers, or the other linear objects, to each other at low temperatures. However, as the temperature is increased to a critical temperature a transition takes place at which they become unbound.

In the case of homopolymers the unbinding transition is fairly well characterized. Using either a directed polymer approach [4] or the more general Poland-Scheraga (PS) type models [5] the nature of the transition and the critical behavior have been studied. In the PS approach, introduced in the context of DNA denaturation, a microscopic configuration of the two polymers is viewed as an alternating sequence of bound segments and denaturated loops. A statistical weight is assigned to each bound segment and open loop. The weight of a bound segment of length l is taken as w^l with $w = \exp(-\beta\epsilon)$, $\beta = 1/(k_B T)$ being the inverse temperature, and ϵ is the binding energy of two monomers. On the other hand a loop of length l is assumed to carry no energy but rather a degeneracy factor which takes the form $\Omega(l) \sim s^l/l^c$. Here s is a geometrical non-universal constant while c is a universal constant.

The nature of the unbinding transition was found to depend only on the parameter c [5]. The transition is continuous for $1 < c \leq 2$ and is first order for $c > 2$. No phase transition takes place for $c \leq 1$ and the polymers are bound at all temperatures. The value of c taken in the PS approach is universal and depends only on the dimension d of the system and on whether or not long range interactions, such as self-avoiding interactions, are taken into account [5, 6, 7]. In the directed polymer approach in $d+1$ dimensions c is related to the number of

random walks which return to the origin for the first time. This is known to be given by [8] $c = 2 - d/2$ for $d < 2$, $c = d/2$ for $d > 2$. In $d = 2$ one has $\Omega(l) \sim s^l/(l \ln^2 l)$.

In many cases one is interested in the unbinding transition of two heteropolymers which are composed of a sequence of two or more types of monomers. This is the case, for example, in DNA where each strand is composed of a sequence of four types of nucleotides. Heteropolymer unbinding is usually modelled by introducing a quenched disorder in the contact energy between the two chains. This disorder, besides modifying the nature of the unbinding transition, may introduce Griffiths singularities in the free energy as is the case in, for example, random magnets [9]. In this Letter we study these singularities in strongly disordered heteropolymer unbinding.

For weak disorder the Harris criterion [10] may be applied in order to determine whether or not the critical behavior of the homopolymer unbinding is modified by the disorder. One finds that weak disorder is irrelevant as long as $c < 3/2$ [11, 12, 13]. This corresponds to $1 < d < 3$ for directed polymers. The marginal $c = 3/2$ case, corresponding to $d = 1$ and $d = 3$ in directed polymers, has been studied in detail [12, 13, 14, 15, 16] and is found to be marginally relevant [13, 14, 15].

Recently the case of strong disorder has been considered by Tang and Chaté [17]. In this study the unbinding transition is analyzed using a real-space renormalization group scheme and numerical studies using a transfer matrix approach. It is suggested that in the strong disorder regime the unbinding transition becomes very smooth, of a Kosterlitz-Thouless (KT) type, with a weak free energy singularity of the form $\exp(-a/\sqrt{|T - T_M|})$ for $T < T_M$. The free energy is differentiable to all orders at $T = T_M$. On the other hand, an analysis of the transition by Azel [18] suggests that the transition could be of very high but finite order (over 100). The order of the transition depends on non-universal quantities like the details of the distribution of the binding energies.

In this Letter we introduce a simple model for the unbinding process of heteropolymers in the strong disorder regime. We demonstrate that the free energy exhibits a Griffiths type singularity [9, 19, 20, 21] at a low tempera-

ture, T_G , resulting from the melting of long homogeneous domains of sites with low binding energy. The model then exhibits an unbinding transition at a higher temperature, T_M .

The model considered in this study is a PS model with two types of randomly distributed binding sites. The energy ϵ_i of site i is given by:

$$\epsilon_i = \begin{cases} -1 & , \text{ with probability } p \\ -v & , \text{ with probability } 1 - p \end{cases} \quad (1)$$

We first study the limit $v \rightarrow \infty$, where no unbinding takes place. We demonstrate that a Griffiths singularity occurs at a temperature $T_G = O(1)$. We then argue that the transition persists at finite but large v , where it is followed by an unbinding transition at a higher temperature $T_M = O(v)$. This model is similar in spirit to a class of models used in the past to study, for example, random field Ising models [22].

The simplifying feature of the limit $v \rightarrow \infty$ is that the chain is decomposed into independent non-interacting finite segments. The free energy of the model is thus obtained by properly averaging the free energy of finite segments, each of which is homogeneous. The free energy density of the chain may thus be expressed as

$$\mathcal{F} = (1 - p)^2 \sum_{N=0}^{\infty} p^N f_N(t) . \quad (2)$$

Here $t = (T_G - T)/T_G$, where T_G is the melting temperature of a homopolymer with $\epsilon = -1$. The free energy density $f_N(t)$ is that of a homogeneous chain of length $N + 2$ where the first and last sites of the two stands are taken to be bound. In the thermodynamic limit the singular part of the free energy is given by [6]

$$\lim_{N \rightarrow \infty} f_N(t) \sim \begin{cases} 0 & , \quad t < 0 \\ t^\nu & , \quad t > 0 \end{cases} \quad (3)$$

where ν is the critical exponent associated with the divergence of the correlation length $\xi \sim t^{-\nu}$. The exponent is given by [6]

$$\nu = \begin{cases} 1/(c - 1) & , \text{ for } 1 < c \leq 2 \\ 1 & , \text{ for } c > 2 \end{cases} \quad (4)$$

Clearly, at any finite N , $f_N(t)$ is an analytic function of t and the singularity develops only in the limit $N \rightarrow \infty$. The sum (2) is a canonical case where Griffiths type singularities may arise.

We proceed by first demonstrating that the average free energy (2) is singular at $t = 0$. This is done by showing that $t = 0$ is an accumulation point of the poles of the free energy in the complex t plane. The average

free energy is then proved to be differentiable to all orders at the transition.

To show that the free energy (2) is singular at $t = 0$, we use the Lee-Yang theory [23] and analyze $f_N(t)$ in the complex $w = \exp(\beta)$ plane for large N . The partition sum $Z_N(w)$ of a finite chain is a polynomial of order N or less in the complex $w = w_R + iw_I$ plane. It has no zeros on the positive real w axis. Let $\rho_N(w_R, w_I)$ be the density of zeros in the complex w plane. The free energy density $f_N(w)$ may be expressed as

$$f_N(w) = -\frac{1}{\beta N} \int \rho(x, y) \ln(w - z) dx dy \quad (5)$$

where $z = x + iy$. To calculate $\rho(x, y)$ we note that it can be expressed as [23, 24]

$$\rho(x, y) = 2\pi \nabla^2 \phi , \quad (6)$$

with

$$\phi = \lim_{N \rightarrow \infty} \frac{\ln |Z_N|}{N} . \quad (7)$$

One may thus view $-\phi$ as an electrostatic potential in a two-dimensional space generated by a charge density $\rho(x, y)$. We proceed by calculating ϕ near the transition where $w - w_G \propto t$. It is evident from Eq. (3) that the system exhibits two phases: an unbound phase (I) near the real negative t axis where $Z_N = 1$ and a bound phase (II) near the real positive t axis where $Z_N = \exp(Nt^\nu)$. In the complex t plane the potential in the two phases is

$$\phi(t) = \begin{cases} 0 & , \text{ phase I} \\ r^\nu \cos(\theta\nu) & , \text{ phase II} \end{cases} \quad (8)$$

where $t = r \exp(i\theta)$. The boundary between the two phases is found by requiring that ϕ is continuous. This yields the lines $\theta = \pm\pi/(2\nu)$. Hence phase II exists inside the wedge $-\pi/(2\nu) < \theta < +\pi/(2\nu)$ while phase I exists on the outside (see Fig. 1). The discontinuity in the field $\vec{E} = \nabla\phi$ in the direction perpendicular to the phase boundary yields the charge density and thus the density of zeros of the partition sum on that line. The angular component of the electric field $E_\theta = 1/r \partial_\theta \phi$ in phase II on the transition lines $\theta = \pm\pi/(2\nu)$ is given by

$$E_\theta = \mp \nu r^{\nu-1} . \quad (9)$$

Thus, the density of the zeros of the partition sum along these lines in the $N \rightarrow \infty$ limit is

$$\rho(r) = \frac{\nu}{2\pi} r^{\nu-1} . \quad (10)$$

It is evident that for $c > 2$, where $\nu = 1$, the density of zeros is constant. Thus the typical distance r_0 to the first zero is of order $r_0 \sim 1/N$. For $1 < c < 2$, where $\nu = 1/(c-1)$, the density of zeros vanishes as $t \rightarrow 0$. The

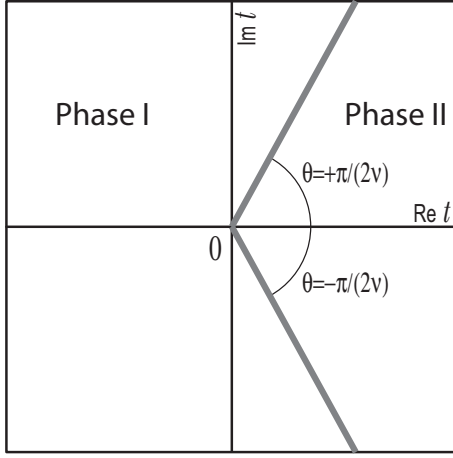


FIG. 1: A schematic illustration of the lines (in gray) in the complex t plane on which the Lee-Yang zeros of the partition sum lie. The density of zeros on these lines satisfies $\rho \sim r^{\nu-1}$.

typical distance, r_0 , is determined by $\int_0^{r_0} r^{\nu-1} dr \sim 1/N$. This yields $r_0 \sim 1/N^{c-1}$. Note that this distance goes to zero in the thermodynamic limit as long as $c > 1$. On the other hand for $c < 1$, r_0 does not vanish in the thermodynamic limit and thus no singularity develops in the partition sum and no transition takes place, as expected.

We have checked this picture by numerically evaluating the zeros of the partition sum of a simple model of a directed polymer in 1+1 dimension corresponding to $c = 3/2$. In this model we consider a random walk which at each step moves either up ($x \rightarrow x+1$) or down ($x \rightarrow x-1$) with probability 1/2. We consider walks of length N such that $x_0 = x_N = 0$ for which $x \geq 0$ at all intermediate steps. With each visit to the origin, $x = 0$, we associate a weight w . The partition sum of this model is

$$Z_N = \sum_{R=1}^{N/2} w^R Q_{N,R}, \quad (11)$$

where $Q_{N,R} = \frac{R}{N-R} \binom{N-R}{N/2}$ is the number of such walks of length N which return to the origin R times [25]. It is straightforward to show that in the $N \rightarrow \infty$ limit, the model undergoes a transition at $w = 2$. The zeros of the partition sum (11) have been calculated numerically for $N = 100$ and $N = 380$ and are shown in Fig. 2. It is readily seen that the zeros are located on a curve in the complex w plane. As N increases this curve develops a wedge near $w = 2$. In the large N limit the curve should approach the point $w = 2$ at an angle $\theta = \pm\pi/4$.

We now turn to the average free energy density \mathcal{F} , Eq. 2. It is clear that $t = 0$ is an accumulation point of the poles of this free energy (or equivalently of the zeros of the corresponding partition sum). Thus the series expansion of the free energy at $t = 0$ has a zero radius of convergence and the free energy is singular. However, this singularity

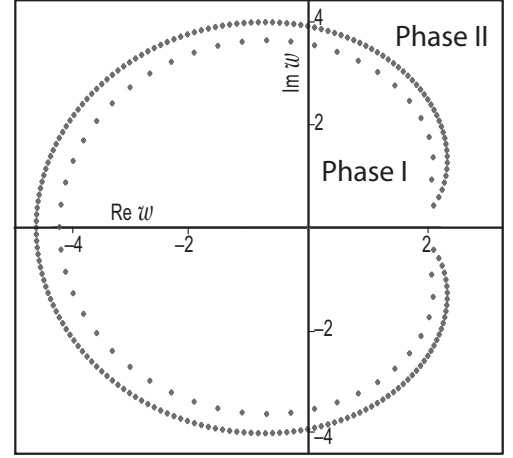


FIG. 2: The Lee-Yang zeros of the partition sum (11) for a direct walk model corresponding to $c = 3/2$ are shown for $N = 100$ (inner points) and $N = 380$ (outer points).

is expected to be rather weak since the weight of the poles located at a distance $O(1/N^{1/\nu})$ from $t = 0$ (which correspond to $f_N(t)$ in (2)) have an exponentially small weight p^N . This is a typical case of a Griffiths singularity.

To demonstrate that the average free energy $\mathcal{F}(t)$ is differentiable to all order at $t = 0$ we adopt the approach of [21] used for analyzing the Griffiths singularities in random ferromagnets. We start by considering the m th derivative of $f_N(t)$

$$\begin{aligned} \frac{\partial^m f_N}{\partial \beta^m} = & \\ -\frac{1}{\beta N} \sum_{\{k_i\}} A(k_1, k_2, \dots, k_l) \langle |E|^{k_1} \rangle \langle |E|^{k_2} \rangle \dots \langle |E|^{k_l} \rangle, & \end{aligned} \quad (12)$$

where the sum over $\{k_i\}$ is taken with the constraint $k_1 + k_2 + \dots + k_l = m$ and E is the energy of a chain of length $N + 2$ with the first and last sites bound. The brackets denote a thermal average. The coefficients $A(k_1, k_2, \dots, k_l)$ are combinatorial factors independent of the system size N . Since the energy at each site is either -1 (bound site) or 0 (unbound site), one has on the real t axis $\langle |E|^k \rangle \leq N^k$. Thus

$$\left| \frac{\partial^m f_N}{\partial \beta^m} \right| \leq \frac{N^{m-1}}{\beta} \left| \sum_{\{k_i\}} A(k_1, k_2, \dots, k_l) \right|. \quad (13)$$

This inequality may be written as

$$\left| \frac{\partial^m f_N}{\partial \beta^m} \right| \leq \frac{1}{\beta} g(m) N^{m-1} \quad (14)$$

where $g(m)$ is independent of N and β . We now consider the m th derivative of the average free energy \mathcal{F} ,

$$\frac{\partial^m \mathcal{F}}{\partial \beta^m} = (1-p)^2 \sum_{N=0}^{\infty} p^N \left(\frac{\partial^m f_N}{\partial \beta^m} \right). \quad (15)$$

It is evident from (14) that this series converges absolutely which allows us to interchange the order of the derivative and the sum. In fact, on the real t axis the m th derivative of \mathcal{F} is bounded by

$$\left| \frac{\partial^m \mathcal{F}}{\partial \beta^m} \right| \leq (1-p)^2 g(m) \sum_{N=1}^{\infty} p^N N^{m-1} \\ \sim (1-p)^2 g(m) \frac{\Gamma(m)}{|\ln p|^m}, \quad (16)$$

where $\Gamma(m)$ is the Gamma function. Therefore the derivative exists on the real t axis and particularly at $t = 0$. This analysis implies that the average free energy is differentiable to all order in β at $t = 0$.

An insight of the singularity of the free energy may be obtained by considering only the poles closest to $t = 0$ in $f_N(t)$ for calculating \mathcal{F} . For example for $c > 2$ these poles are located at $t = \pm ib/N$, where b is a constant. Approximating the sum on N in (2) by an integral and after rescaling t one finds

$$\mathcal{F} \propto -\frac{1}{\beta} \int_0^{\infty} e^{-x} \ln(x^2 t^2 + 1) dx. \quad (17)$$

This integral is singular at $t = 0$ as expected.

So far we analyzed the limit $v \rightarrow \infty$, where no unbinding takes place. Let us now consider finite v with $v \gg 1$. In this case the model is expected to exhibit an unbinding transition at $T_M = O(v)$, in addition to the Griffiths singularity at T_G . This may be seen by noting that at low temperatures, $T \geq T_G$, the two polymers are expected to be bound even for finite but large v . The reason is that the free energy difference between the state which is bound at all strongly binding sites and the completely unbound state is

$$\Delta F = -pvL + TpLu \ln s, \quad (18)$$

where u is a constant of $O(1)$, $\ln s$ is the entropy density of a random walk and L is the polymer length. Clearly the second, entropic, term is negligibly small at $T \ll v$. Thus the polymers are expected to be bound at low temperatures with an unbinding transition taking place at $T_M = O(v)$.

The fact that v is finite but large is not expected to modify the nature of the Griffiths singularity found for $v \rightarrow \infty$ at $T = T_G$. At finite v some of the strongly binding sites may become unbound even at the low temperature around T_G . However this effect is small and is not expected to modify the exponential behavior of the domain size distribution taken in (2). For $T > T_G$ where all homogeneous domains are unbound our model is closely related to the Tang-Chaté model in which the melting transition has been analyzed. Their analysis of the melting transition should be applicable to the melting transition in this model as well.

In summary, we have demonstrated that the model considered in this study exhibits a Griffith singularity in the limit of infinitely strong binding sites $v \rightarrow \infty$. It is argued that this transition is present even for finite but large v , where it is followed at a higher temperature by an unbinding transition.

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